

387-nm Generation in $Gd_xY_{1-x}Ca_4O(BO_3)_3$ Crystal and Its Utilization for 193-nm Light Source

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We report on near-UV generation in $Gd_xY_{1-x}Ca_4O(BO_3)_3$ crystals used under type-I non-critical phase-matching conditions. $Gd_xY_{1-x}Ca_4O(BO_3)_3$ was also applied to a 193-nm deep-UV laser source based on the eighth harmonic of an erbium-doped fiber amplifier output at 1547 nm, in which $Gd_xY_{1-x}Ca_4O(BO_3)_3$ ($x = 0.68$) was used for 387-nm generation. Using this compact light source, 5% conversion efficiency from the 1547-nm input to the 193-nm output was achieved at a fundamental peak power of 18 kW. [DOI: 10.1143/JJAP.42.L166]

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In recent years, rare-earth calcium oxyborate $Re-Ca_4O(BO_3)_3$ (Re: rare-earth atoms) materials have received a great deal of attention as promising nonlinear optical (NLO) crystals. These materials possess moderate optical nonlinearity, nonhygroscopicity, and sufficient mechanical hardness. In addition, it is relatively easy to grow large crystals by the Czochralski method. It has been reported that $GdCa_4O(BO_3)_3$ (GdCOB), $YCa_4O(BO_3)_3$ (YCOB) and a substitutional solid solution of $Gd_xY_{1-x}Ca_4O(BO_3)_3$ (GdYCOB) are suitable for blue to near-UV generation.^{1–5)} GdYCOB crystal is unique in that its birefringence is tunable by controlling the composition ratio of Gd to Y. For type-I second harmonic generation (SHG) along the y-axis, the non-critical phase-matching (NCPM) wavelength of the fundamental light is 831 nm in GdCOB and 725 nm in YCOB. By adjusting the compositional parameter x , GdYCOB can realize any NCPM wavelength between the above-mentioned values. We focused on 387-nm generation, the half frequency of a 193-nm ArF excimer laser, to utilize GdYCOB crystal for an all-solid-state 193-nm light source.

Deep-UV laser sources, particularly those operating at 193 nm, have been in great demand for a variety of applications. In addition to the ArF excimer laser, several different solid-state 193-nm laser systems have been demonstrated.^{6–8)} We have reported the first 193-nm source using eighth-harmonic generation (8HG) from the output of an erbium-doped fiber amplifier (EDFA) at 1547 nm.⁶⁾ Five stages of frequency conversion were used in this source to obtain 193-nm output as schematically depicted in Fig. 1(a). A further compact, stable, and efficient frequency-conversion setup is demanded for practical applications. The best method is to reduce the number of NLO crystals by a direct

SHG process from 387 nm to 193 nm if possible, realizing a three-stage conversion process. However, NLO crystals that can generate 193-nm light by SHG have not been commercially available up to now. β -BaB₂O₄ (BBO) crystal has a large birefringence and can provide 193-nm output by a sum frequency of the 773-nm second harmonic and the 258-nm sixth harmonic; it can reduce one stage of frequency conversion in a five-stage system. However, BBO crystal is not transparent enough at 193 nm, which decreases the durability of the crystal. Consequently, LiB₃O₅ (LBO) and CsLiB₆O₁₀ (CLBO) are the only practically useful NLO crystals that can generate 193-nm light. Since these crystals do not have a large birefringence, sum frequency generation processes with the fundamental and the 221-nm seventh harmonic are required to obtain a 193-nm output.

In this work, we adopted another approach, GdYCOB for 387-nm fourth-harmonic generation (4HG) under the NCPM condition. In the previous work, LBO was used for 4HG under a critical phase-matching (CPM) condition. Figure 1 illustrates the difference between the two setups. Because of the NCPM nature of GdYCOB, a simpler optical path can be realized. We demonstrate a 193-nm light source incorporating GdYCOB and compare its characteristics to those of a conventional LBO-based source.

The frequency conversion process used for 193-nm generation is described in Table I, and its setup is shown in Fig. 1, together with its fundamental light source. The fundamental light source at 1547 nm consists of a directly modulated, distributed-feedback laser diode (DFB-LD) and an EDFA system. The EDFA amplifies the optical pulses generated by the DFB-LD with a total gain exceeding 60 dB. The fundamental source provides output pulses of a beam

Table I. Frequency conversion process for 193-nm generation.

Process	SHG	THG	4HG		7HG	8HG
Wavelength	773 nm	516 nm	387 nm		221 nm	193 nm
Interaction	$\omega + \omega$	$\omega + 2\omega$	$2\omega + 2\omega$		$3\omega + 4\omega$	$\omega + 7\omega$
Crystal	LBO	LBO	LBO	GdYCOB	BBO	CLBO
PM angle (θ, ϕ)	(90°, 0°)	(90°, 0°)	(90°, 34.4°)	(90°, 90°)	(64.7°,)	(61.7°,)
d_{eff} (pm/V)	0.85	0.85	0.70	0.55	1.01	0.83
Walk-off (mrad)	0	0	17.4	0	70.7	38.7
Crystal Temp.	117°C	141°C	RT	240°C	RT	150°C

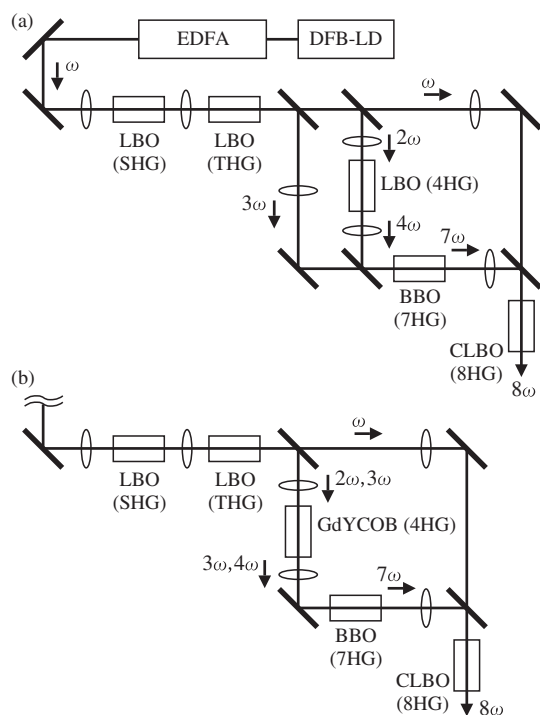


Fig. 1. Experimental setups for 193-nm generation. Five stages of frequency conversion are used to obtain the eighth harmonic light from the EDFA output of 1547 nm. The 4HG is performed by LBO in the conventional setup (a) and by GdYCOB in the new setup (b). The NCPM frequency conversion in GdYCOB can realize simpler optical path for 8HG.

quality of $M^2 < 1.1$, a linewidth of less than 0.1 nm, and pulse duration of approximately 1 ns at a repetition rate of 1 kHz. The second and third harmonics of the fundamental beam are generated using LBO crystals under temperature-controlled NCPM conditions. The second harmonic is injected into GdYCOB (Fig. 1(b)) or LBO (Fig. 1(a)) to generate the fourth harmonic. The seventh harmonic generation (7HG) is performed as the sum frequency of the third and fourth harmonic using a BBO crystal at room temperature (RT). Finally, the fundamental and the seventh harmonic are mixed to produce 8HG in a CLBO crystal. All crystals are used under type-I phase-matching (PM) conditions.

In this study, each harmonic is tightly focused in the crystal to enhance conversion efficiency since the fundamental light has a maximum pulse energy of approximately 20 μ J. Because the beam sizes are small, we must carefully consider walk-off effects in the crystals. The experimental scheme for 4HG and 7HG greatly depends on whether the 4HG process is or is not NCPM.

When LBO is used for 4HG (Fig. 1(a)), the walk-off in LBO distorts the fourth-harmonic beam shape. An anamorphic optical system is required to reshape the fourth-harmonic beam profile. In contrast, the 516-nm third-harmonic beam generated by the NCPM process has an undistorted round profile. Therefore, the third- and the fourth-harmonic light should be relayed to the fourth-stage (7HG) BBO crystal with different beam-shaping optics. The second harmonic and the third harmonic were spatially separated after third-harmonic generation (THG). We used cylindrical lenses for the fourth-harmonic reshaping,

whereas the third harmonic was relayed with the spherical lenses.

In contrast, by using GdYCOB (Fig. 1(b)), the NCPM condition is applicable to the 4HG stage in addition to the SHG and THG stages. Namely, the cylindrical beam shapers are unnecessary in the fourth-harmonic path. This makes it possible for the third-harmonic beam to pass through GdYCOB coaxially with the second- and fourth-harmonic beams. Consequently, we can construct a miniaturized, simple setup for 7HG.

GdYCOB single crystals examined in all our measurements were grown by the RF-heated Czochralski technique using an iridium crucible. The starting materials were prepared by sintering of 4N pure Gd_2O_3 , Y_2O_3 , CaCO_3 and 3N-up B_2O_3 . The mixture was heated to 1100°C for 24 hours, cooled, crushed, and then heated again to 1150°C for 24 hours. The crystal-growth experiments were carried out with a 1 to 4 mm/h pulling rate along the b-axis and 10 to 15 rpm rotation rate, in an Ar atmosphere.

We first measured the type-I NCPM wavelength for various GdYCOB crystals by using a tunable Ti:Sapphire laser. The experiments were carried out at RT. Figure 2 shows the NCPM wavelengths for type-I SHG along the y-axis ($\theta = \phi = 90^\circ$) as a function of the compositional parameter x . The experimental plots at $x = 0$ and $x = 1$ are quoted from ref. 4. The dashed line presents the theoretical curve calculated with the equations reported by Umemura *et al.*³⁾ The experimental values agree relatively well with the calculated values.

An important point in utilizing GdYCOB for UV sources is to avoid photo-induced damage (photo-refractive damage and gray-track) in the crystal. Previous works have revealed that photo-induced damage limits UV output power generated by GdYCOB.²⁾ Although the photo-refractive damage is invisible, it produces a change in the refractive index. The gray-track is visible and is observed as the brown coloring, which gives rise to self-heating of the crystal in the laser-beam propagation. Thus both damages lead to phase mismatching in GdYCOB. This problem can be suppressed by elevating the crystal temperature in some part. According to the calculation in Fig. 2, GdYCOB with $x = 0.71$ is expected to achieve the NCPM wavelength of 773 nm for type-I SHG at RT. However, high-temperature operation is

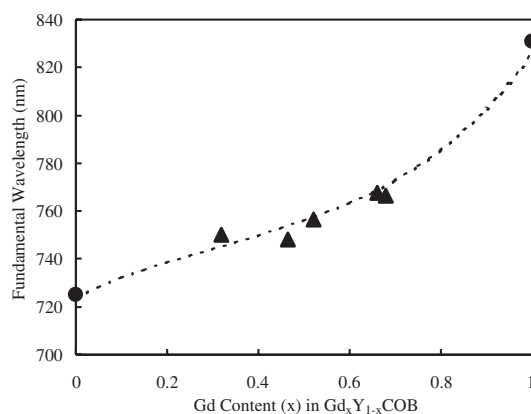


Fig. 2. Relationship between Gd content in GdYCOB and type-I NCPM wavelengths along the y-axis at room temperature.

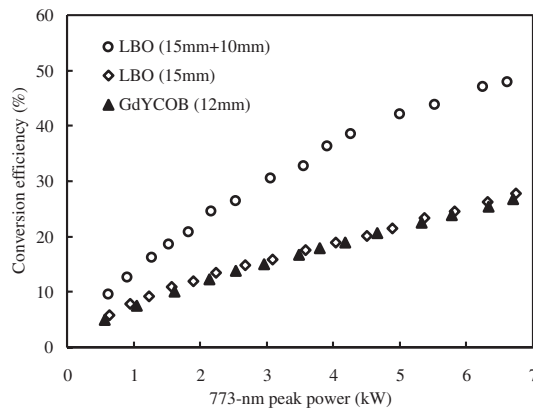


Fig. 3. Conversion efficiency from the second harmonic to the fourth harmonic as a function of the second-harmonic peak power incident to the 4HG crystals.

favorable for efficient UV generation. Therefore, we prepared GdYCOB with $x = 0.68$ for 387-nm generation in order to provide high-temperature NCPM. The NCPM wavelength shifts toward the longer side as the crystal temperature rises.⁵⁾ The measured NCPM temperature of this crystal was 240°C.

We have compared GdYCOB (Fig. 1(b)) and LBO (Fig. 1(a)) used for the 4HG crystals, in our experiments of 193-nm generation. A 12-mm-long GdYCOB crystal was cut along the y -axis, optically polished, uncoated, and heated to 240°C (Fig. 1(b)). While, a single 15-mm-long LBO, or a walk-off compensated LBO pair (15 mm and 10 mm) was employed at RT (Fig. 1(a)). In two cases of LBO setup, LBO crystals were cut for CPM conditions ($\theta = 90^\circ$, $\phi = 34.4^\circ$) and AR-coated. Figure 3 depicts the conversion efficiency of GdYCOB and LBOs as a function of the second-harmonic peak power incident to the 4HG crystals. The efficiency of the 12-mm-long GdYCOB was almost the same as that of the single 15-mm-long LBO. The best data was obtained by the walk-off compensated LBO pair. We should note that the beam profile of the fourth-harmonic output differed considerably between the cases. NCPM frequency conversion in GdYCOB resulted in superior fourth-harmonic beam profiles.

The GdYCOB crystals with different lengths were also examined to investigate 4HG characteristics in detail. Despite the advantage of NCPM expected in the conversion-efficiency enhancement by a long crystal, the fourth-harmonic output by the 16-mm-long GdYCOB was inferior to that by the 12-mm-long GdYCOB. The output of the 10-mm-long GdYCOB was nearly equal to that of the 12-mm-long GdYCOB. This behavior seems to be due to the photo-induced damages that occurred in GdYCOB and Gd/Y-concentration non-uniformity along the y -axis. Both effects are responsible for a decrease in the effective crystal length that contributes to the 4HG.

We evaluated the influence of photo-induced damage by measuring the transmittance of the third harmonic light in GdYCOB. When second harmonic light with a peak power of 6.7 kW was injected into the 12-mm-long GdYCOB, which generated the fourth harmonic with a peak power of 1.8 kW, the third-harmonic transmittance dropped by about 10% compared with the no-4HG condition. The photo-

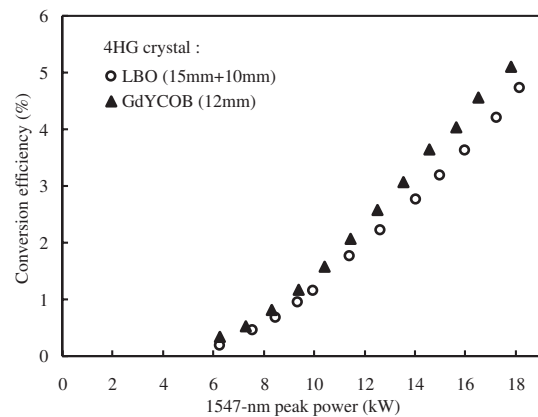


Fig. 4. Conversion efficiency from the fundamental to the eighth harmonic as a function of the fundamental peak power incident to the first-stage LBO crystal.

induced damage was not completely eliminated under the 240°C operation. This reduction seems to originate from gray-track formation in GdYCOB caused by high-intensity UV propagation. The gray-tracked GdYCOB has a broad absorption from UV to visible light.²⁾ However, the coloring induced by the fourth-harmonic propagation was a reversible process. By annealing the crystal at 300°C for several hours, we observed the recovery of transmittance to the original level. The gray-track properties observed in 387-nm generation are consistent with the data of 355-nm generation reported previously.

The beam distortion of the fourth-harmonic output affects performance of the post-4HG frequency-conversion stages. For GdYCOB (Fig. 1(b)), improved conversion efficiencies in the 7HG and 8HG process were observed. Figure 4 presents conversion efficiencies from the fundamental to the eighth harmonic as a function of the fundamental peak power. Although the fourth-harmonic output produced by LBOs (15 mm and 10 mm) was larger than that produced by GdYCOB (12 mm), the setup including GdYCOB surpassed the LBO-based setup at 193-nm output. This means high-efficiency 7HG and 8HG were realized in the GdYCOB setup, which resulted from the better beam profile of 4HG. By using GdYCOB for 4HG, a 5% conversion efficiency from the fundamental to the eighth harmonic was achieved at an input fundamental peak power of 18 kW. In Fig. 4, we should note that the 193-nm output power changes almost linearly with the fundamental power, near the maximum power level. This power dependency can be attributed to the depletions of the fundamental and intermediate harmonic lights. It also indicates that the power of the 193-nm light can be controlled easily by adjusting EDFA output.

In summary, we demonstrated 387-nm generation in a GdYCOB crystal and reported on a 193-nm light source based on the 8HG of the EDFA output, in which GdYCOB was applied to the NCPM 4HG. Although local conversion efficiency in GdYCOB from 773 nm to 387 nm was still lower than that in LBO, the GdYCOB-based 193-nm source had better conversion efficiency than the LBO-based source from the fundamental to the 193-nm output. This results from good beam quality after the NCPM frequency conversion in 4HG. When more uniform, damage-free GdYCOB is available, higher conversion efficiency will be achieved. In

addition, by adopting a high-power erbium-doped amplifier, which enables high repetition pulse amplification with an average power of a few watts, this system has the potential to provide over one hundred milliwatts power at 193-nm output.

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